

WHAT IS CLAIMED IS:

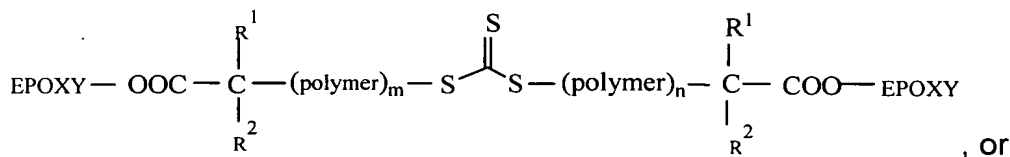
1. A vinyl ester toughener, comprising:

the reaction product of a toughener polymer or copolymer and an

unsaturated monocarboxylic acid;

said unsaturated acid being a monoacid containing from 3 to about 10 carbon atoms;

said toughener polymer having the formula

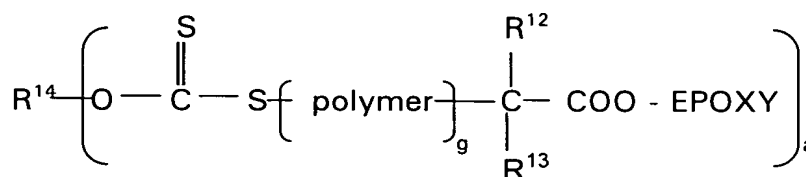


Formula X^I

wherein R¹ and R², independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents, independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

wherein m and n, independently, is a repeat unit of from about 5 to about 1,000; or

said toughener polymer or copolymer having the formula:



Formula H^I

wherein R¹² and R¹³, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing

heteroatoms; or R^{12} and R^{13} can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

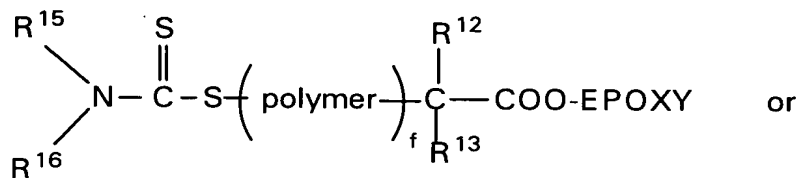
wherein R^{14} is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein said (polymer) is derived from at least one conjugated diene monomer, or a vinyl containing monomer or combinations thereof, with the proviso that each polymer repeat unit can be the same or different;

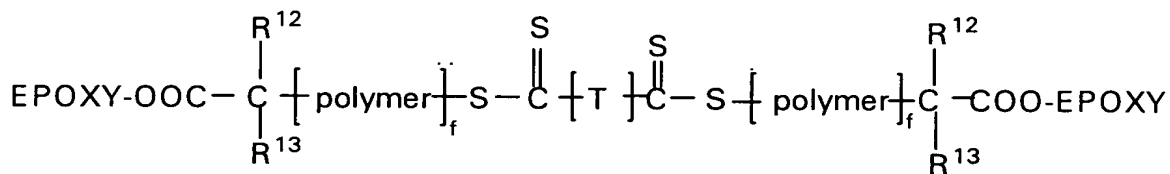
wherein said g is from about 1 to about 10,000; and

wherein said " a " is 1 to about 4; or

said toughener polymer or copolymer being a dithiocarbamate having the formula:



Formula F^I



Formula G^I

wherein each R^{12} and R^{13} , independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to

about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

5 wherein R^{15} and R^{16} , independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3
10 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

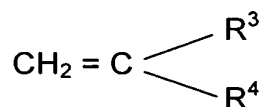
 wherein T is a divalent radical having a nitrogen atom directly
15 connected to each carbon atom of the two thiocarbonyl groups;

 wherein said (polymer) repeat units are derived from at least one conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, with the proviso that each repeat unit can be the same or different; and

20 wherein the number of said repeat units f, independently, is from 1 to about 10,000.

2. A vinyl ester toughener according to claim 1, wherein said Formula X' (polymer), independently, comprises a polyacrylate or polymethacrylate
25 derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl has from 1 to about 18 carbon atoms, a polymer derived from a vinyl substituted aromatic monomer containing from 8 to about 12 carbon atoms, a polymer derived from a conjugated diene monomer containing from 4 to about 12 carbon atoms, a polymer derived from acrylonitrile, or
30 combinations thereof, or

wherein said Formula H' conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



wherein R³ comprises hydrogen, halogen, C₁ – C₄ alkyl, or substituted C₁ - C₄ alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR⁵), carboxy, acyloxy, aroyloxy(O₂CR⁵), alkoxy-carbonyl(CO₂R⁵), or aryloxy-carbonyl; N-pyrrolidonyl;

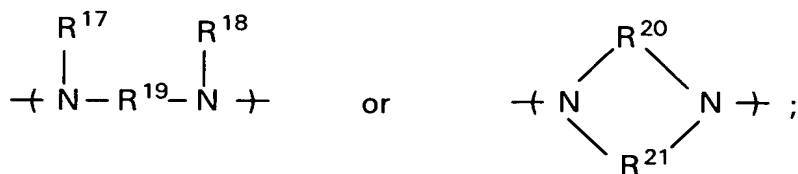
wherein R⁴ comprises hydrogen, R⁵, CO₂H, CO₂R⁵, COR⁵, CN, CONH₂, CONHR⁵, O₂CR⁵, OR⁵ or halogen; and

wherein R⁵ comprises C₁ – C₁₈ alkyl, substituted C₁ – C₁₈ alkyl, C₂ – C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino, and

wherein g is from about 3 to about 5,000; or

wherein in said Formula F' and G' toughener polymer or copolymer f is from about 3 to about 5,000;

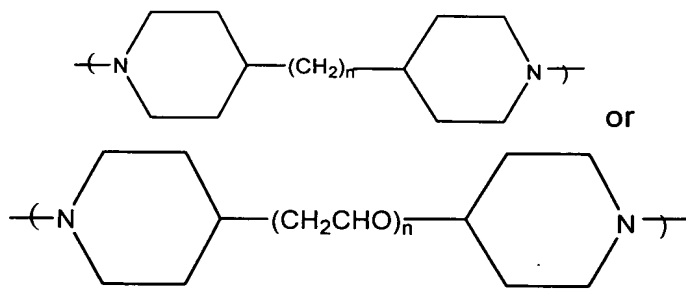
wherein T is:



wherein R¹⁷ and R¹⁸, independently, is the same or different, is optionally substituted, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbon atoms; or an aryl group having from about 6 to about 18 carbon atoms; or an arylalkyl having from 7 to about 18 carbon atoms; or a alkenealkyl having from 3 to about 18 carbon atoms; wherein R¹⁹ is optionally substituted, or is non-existent; or an alkylene group having

from 1 to about 18 carbon atoms; or derived from a polyalkylene glycol either having from 3 to about 200 carbon atoms; wherein R^{20} and R^{21} , independently, is the same or different, and is optionally substituted, and is an alkylene group having from 1 to about 4 carbon atoms, or

5 wherein T is:



wherein n is 0 to about 18.

10 3. A vinyl ester toughener according to claim 2, wherein each said EPOXY, independently, is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin; phenolic novolac epoxy, tetraphenylethane epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from
15 diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epihalohydrin including an epoxy resin derived from unsaturated monoepoxy;
20 epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glycidaldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

25 wherein m and n of Formula X^I, independently, is from about 7 to about 150, and wherein said unsaturated acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof.

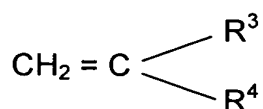
4. A vinyl ester toughener according to claim 3, wherein said Formula X¹ (polymer) is said polyacrylate and said polyacrylate is derived from ethyl acrylate, butyl acrylate, or ethyl-hexyl acrylate, or combinations thereof; wherein
 5 R¹ and R² are methyl; and

wherein said unsaturated acid is acrylic acid or methacrylic acid; and
 wherein the amount of said acid is from about 0.85 to about 1.15 mole equivalents based upon the total mole equivalents of said toughener polymer, or
 wherein, independently, each said polymer repeat unit of Formula H¹ is
 10 derived from alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof, or

wherein R¹² and R¹³, independently, are an alkyl having from 1 to about 4 carbon atoms, or are part of a cyclic ring, and

wherein "a" is 2, and wherein R¹² and R¹³, independently, are a phenyl group or alkyl group having 1 to about 10 carbon atoms, or R¹² and R¹³ are part
 15 of a cyclic ring; or

wherein, independently, in Formulas F¹ or G¹, said conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



wherein R³ comprises hydrogen, halogen, C₁ - C₄ alkyl, or
 25 substituted C₁ - C₄ alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR⁵), carboxy, metal carboxylate (COOM) with M being sodium, potassium, calcium, zinc or an ammonium salt, acyloxy, aroyloxy(O₂CR⁵), alkoxy-carbonyl(CO₂R⁵), aryloxy-carbonyl; or N-pyrrolidonyl;

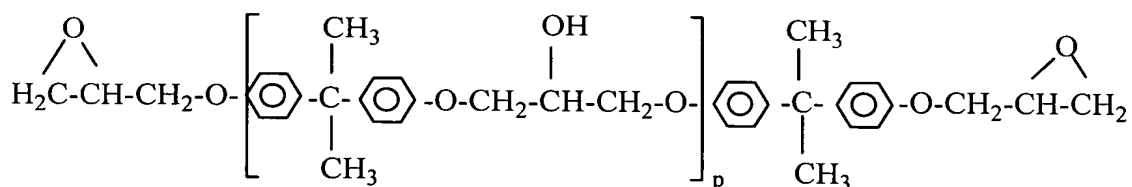
wherein R⁴ comprises hydrogen, R⁵, CO₂H, CO₂R⁵, COR⁵, CN, CONH₂, CONHR⁵, O₂CR⁵, OR⁵ or halogen; and
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wherein R⁵ comprises C₁ – C₁₈ alkyl, substituted C₁ – C₁₈ alkyl, C₂ – C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and

wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, carboxy salts, sulfonic acid, sulfonic salts, alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino.

5. A vinyl ester toughener according to claim 4, wherein in Formula X^I, m and n, independently, are from about 10 to about 200,

wherein each said EPOXY in Formula X^I, F^I, G^I, and H^I, independently, is derived from



wherein p is from 0.1 to about 1.5, and

wherein the number of said terminal EPOXY groups is from about 1 to about 2.

6. A vinyl ester toughener according to claim 5, wherein in said Formulas F^I, G^I, and H^I said (polymer) is a polyacrylate, independently, derived from ethyl acrylate, butyl acrylate, or combinations thereof.

7. A vinyl ester toughener according to claim 1, including an esterification catalyst, and wherein said reaction occurs at a temperature of from about 90°C to about 150°C.

8. A vinyl ester toughener according to claim 3, including an esterification catalyst, and wherein said reaction occurs at a temperature of from about 90°C to about 150°C.

9. A vinyl ester toughener according to claim 5, including an esterification catalyst, and

wherein the reaction occurs at a temperature of from about 105°C to about 135°C.

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10. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 1, and a vinyl ester epoxy,

said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid having from 3 to about 10 carbon atoms.

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11. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 2, and a vinyl ester epoxy;

said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid having from 3 to about 10 carbon atoms;

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wherein said epoxy resin is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin; phenolic novolac epoxy, tetraphenylethane epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epichlorohydrin including an epoxy resin derived from unsaturated monoepoxy; epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glycidaldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

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wherein m and n of Formula X¹, independently, is from about 7 to about 150.

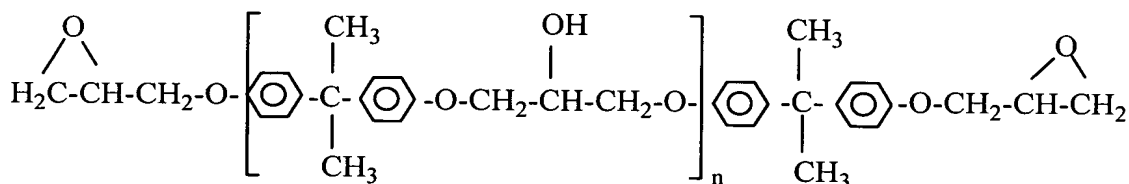
12. A blend of vinyl ester resins, comprising:

5 a vinyl ester toughener of claim 4, and a vinyl ester epoxy;

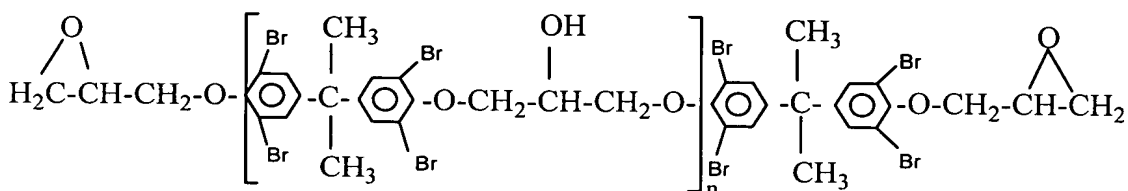
said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

10 wherein the amount of said vinyl ester toughener is from about 1 to about 20 parts by weight per 100 parts by weight of said vinyl ester epoxy;

and wherein each said epoxy resin, independently, is

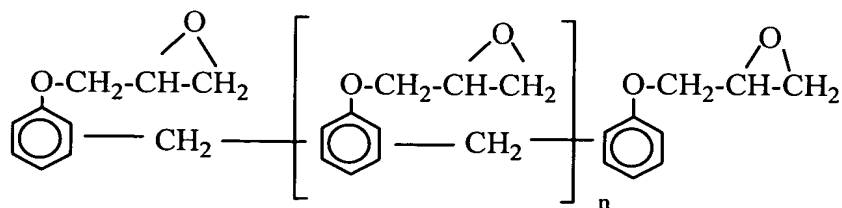


wherein n is an integer from 0 or from about 0.1 to about 18, or;

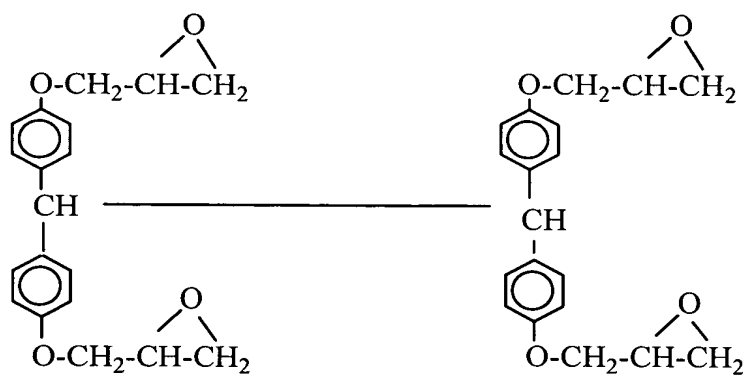


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wherein n is from 0 or about 0.1 to about 18, or



wherein n is from about 0 or about 0.1 to about 8; or



or combinations thereof.

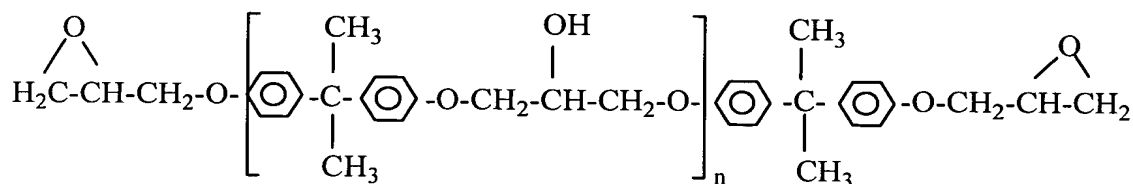
13. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 5, and a vinyl ester epoxy;

said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

wherein the amount of said vinyl ester toughener is from about 1 to about 20 parts by weight per 100 parts by weight of said vinyl ester epoxy;

and wherein each said epoxy resin, independently, is



wherein n is an integer from 0 or about 0.1 to about 1.5.

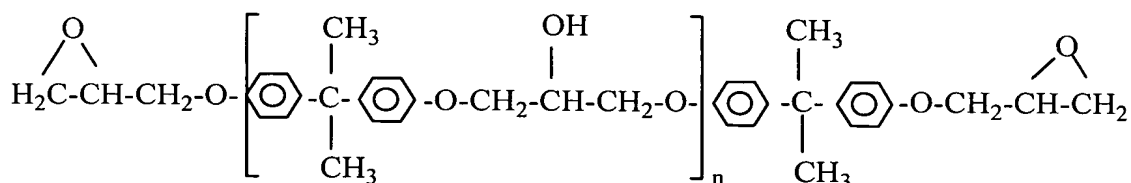
14. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 6, and a vinyl ester epoxy;

said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

wherein the amount of said vinyl ester toughener is from about 2 to about 15 parts by weight per 100 parts by weight of said vinyl ester epoxy;

and wherein each said epoxy resin, independently, is



5 wherein n is an integer from 0 or about 0.1 to about 1.5.

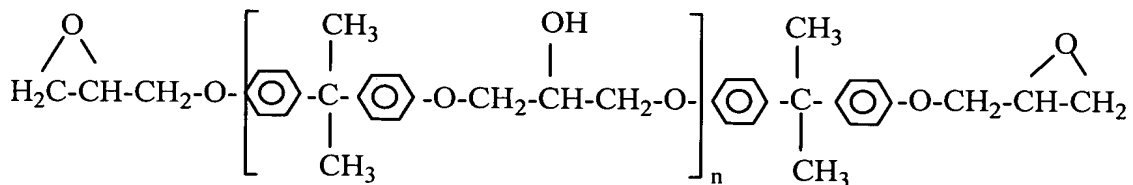
15. A blend of vinyl ester resins, comprising:

a vinyl ester toughener of claim 8, and a vinyl ester epoxy;

10 said vinyl ester epoxy being the reaction product of at least one epoxy resin and a monounsaturated carboxylic acid wherein said monounsaturated carboxylic acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

wherein the amount of said vinyl ester toughener is from about 2 to about 15 parts by weight per 100 parts by weight of said vinyl ester epoxy;

15 and wherein said each epoxy resin, independently, is



wherein n is an integer from 0 or about 0.1 to about 1.5.

20 16. The crosslinked composition of claim 10, including a diluent therein, and optionally including a toughener which is miscible before cure;

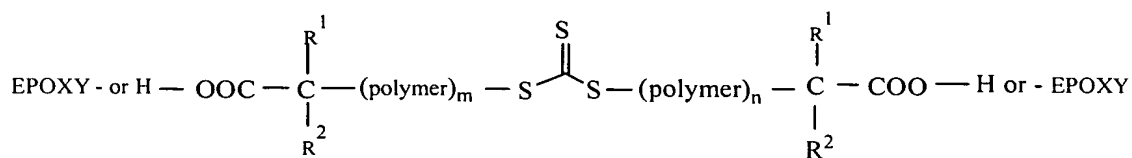
said diluent comprising an unsaturated organic solvent.

17. The crosslinked composition of claim 12, including a diluent, and including a toughener which is miscible before cure;

wherein the amount of said miscible toughener is from about 2 to about 50 parts by weight per 100 parts by weight of said vinyl ester resins

said diluent comprising an unsaturated organic solvent having from 5 to about 15 carbon atoms;

5 wherein said miscible toughener has the formula



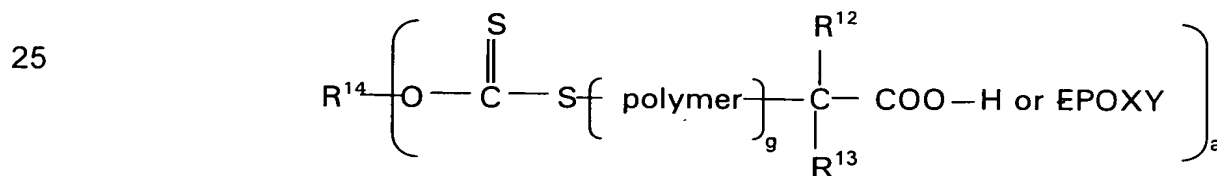
Formula X¹

10 wherein R¹ and R², independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents, independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

15 wherein m and n, independently, is from about 5 to about 1,000,

wherein each said (polymer), independently, comprises a polyacrylate or a polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl has from 1 to about 18 carbon atoms, a polymer derived from a vinyl substituted aromatic monomer containing from 8 to about 12 carbon atoms, a polymer derived from a conjugated diene monomer containing from 4 to about 12 carbon atoms, a polymer derived from acrylonitrile, or combinations thereof; or

a toughener polymer or copolymer having the formula



Formula H¹

wherein R^{12} and R^{13} , independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

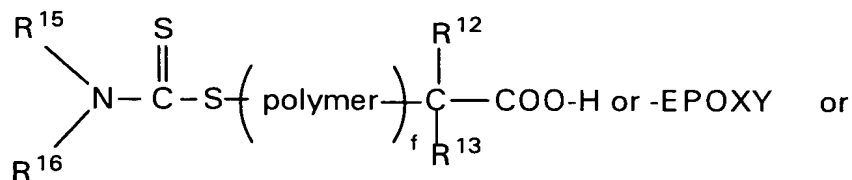
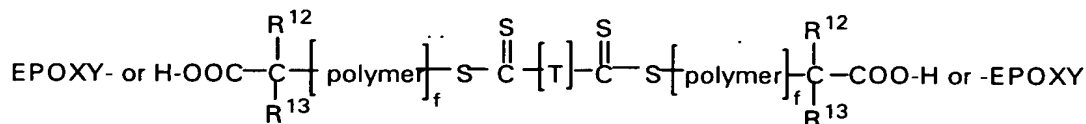
wherein R^{14} is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein the (polymer) is derived from at least one conjugated diene monomer, or a vinyl containing monomer or combinations thereof, with the proviso that each polymer repeat unit can be the same or different;

wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4; or

said toughener polymer or copolymer being a dithiocarbamate having the formula:

Formula F^IFormula G^I

wherein each R^{12} and R^{13} , independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R^{12} and R^{13} can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R^{15} and R^{16} , independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

wherein said (polymer) repeat units are derived from at least one conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, with the proviso that each repeat unit can be the same or different; and

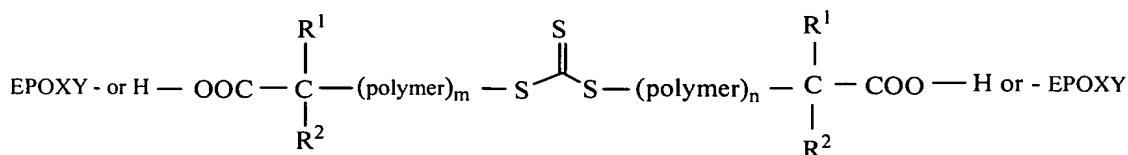
wherein the number of said repeat units f, independently, is from 1 to about 10,000.

18. The crosslinked composition of claim 14, including a diluent therein and including a toughener which is miscible before cure;

said diluent comprising an unsaturated organic solvent having from 5 to about 15 carbon atoms,

wherein said miscible toughener has the formula

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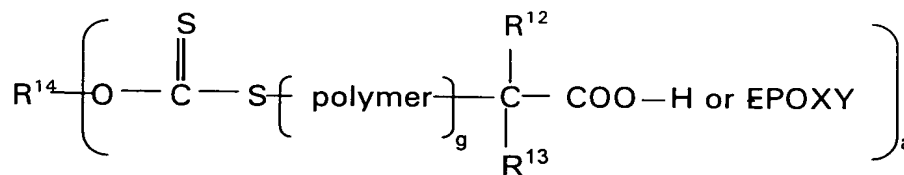
Formula X^I

wherein R¹ and R², independently, are an alkyl having 1 to about 6 carbon atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at least one aryl, or at least one substituted aryl having from 1 to about 6 substituents on the aryl ring, and wherein said one or more substituents, independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or a halogen group, or a cyano group, or an ether having a total of from 2 to about 20 carbon atoms, or a nitro group, or combinations thereof,

wherein m and n, independently, is from about 5 to about 500,

wherein each said (polymer), independently, comprises a polyacrylate or a polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl is ethyl, butyl, or combinations thereof; or

a toughener polymer or copolymer having the formula

Formula H^I

wherein R¹² and R¹³, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R¹² and R¹³ can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

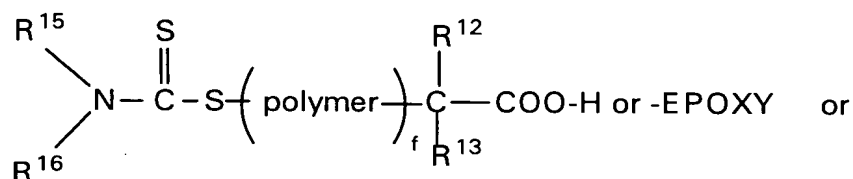
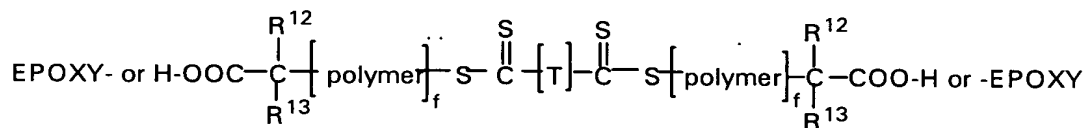
wherein R¹⁴ is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a

polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4; or

said toughener polymer or copolymer being a a dithiocarbamate having the formula:

Formula F^IFormula G^I

wherein each R¹² and R¹³, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R¹² and R¹³ can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R¹⁵ and R¹⁶, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or

derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

wherein T is a divalent radical having a nitrogen atom directly
5 connected to each carbon atom of the two thiocarbonyl groups;

wherein the number of said repeat units f, independently, is from 1 to about 10,000;

wherein said (polymer) of said Formulas H^I , F^I and G^I , independently, is a polyacrylate derived from an alkyl acrylate or alkyl methacrylate monomer
10 wherein said alkyl is ethyl acrylate, butyl acrylate, or ethyl-hexyl acrylate, or combinations thereof; and

wherein said EPOXY of said miscible toughener of said Formulas H^I , F^I and G^I , independently, is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin; phenolic novolac epoxy, tetraphenylene oxide epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of
15 bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine
20 glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epichlorohydrin including an epoxy resin derived from unsaturated monoepoxy; epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glycidaldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized
25 from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

wherein said unsaturated acid is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, or combinations thereof;

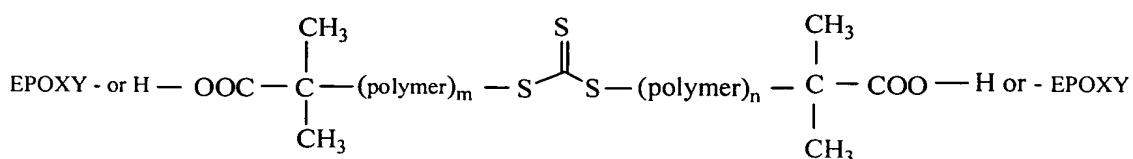
wherein the amount of said miscible toughener is from about 2 to about
30 25 parts by weight per 100 parts by weight of said vinyl ester resins; and

wherein said miscible toughener exists as a discontinuous phase within said crosslinked composition.

19. The crosslinked composition of claim 16, including a diluent therein and including a toughener which is miscible before cure;

said diluent comprising styrene, α -methylstyrene, or methacrylate, or an acrylate, or combinations thereof;

wherein said miscible toughener has the formula

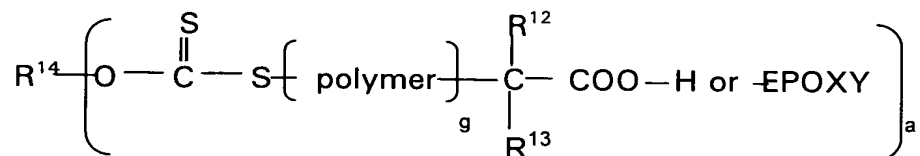


Formula X^I

wherein m and n, independently, is from about 5 to about 200,

wherein each said (polymer), independently, comprises a polyacrylate or a polymethacrylate derived from an alkyl acrylate or alkyl methacrylate monomer wherein said alkyl is ethyl, butyl, or combinations thereof; or

a toughener polymer or copolymer having the formula



Formula H^I

wherein R¹² and R¹³, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R¹² and R¹³ can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R¹⁴ is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3

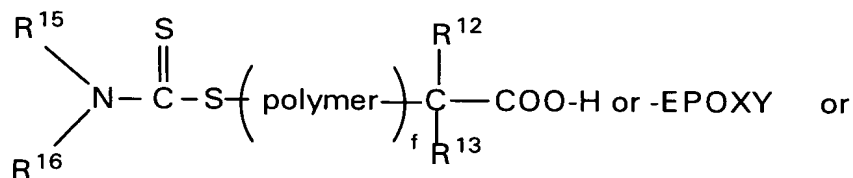
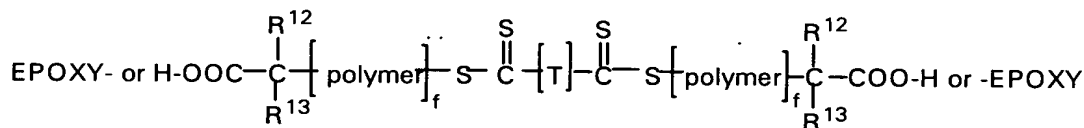
to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4;

wherein, independently, each said (polymer) repeat unit of Formula H^I is derived from an alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof, or

said toughener polymer or copolymer being a dithiocarbamate having the formula:

Formula F^IFormula G^I

wherein each R¹² and R¹³, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R¹² and R¹³ can form and be part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

wherein R¹⁵ and R¹⁶, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or

branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or
 5 derived from an amine; or R^{15} and R^{16} are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

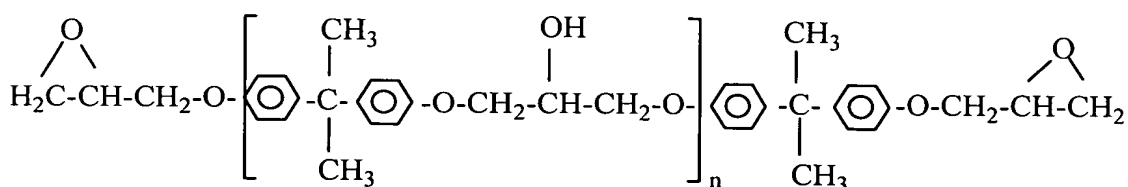
10 wherein the number of said repeat units, independently, is from about 3 to about 5,000;

wherein, independently, each said (polymer) repeat unit of Formulas F¹ and G¹ is derived from an alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof; and

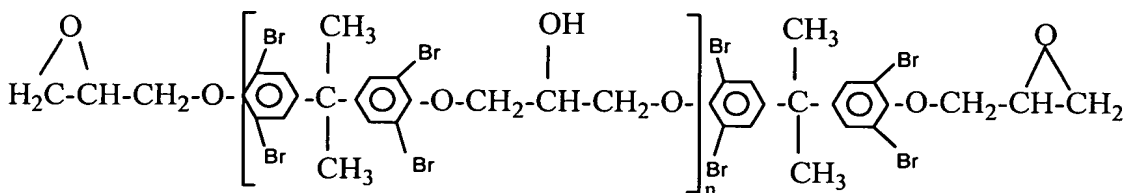
15 wherein the amount of said miscible toughener is from about 4 to about 10 parts by weight per 100 parts by weight of said vinyl ester resins;

wherein said unsaturated acid is acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, or combinations thereof;

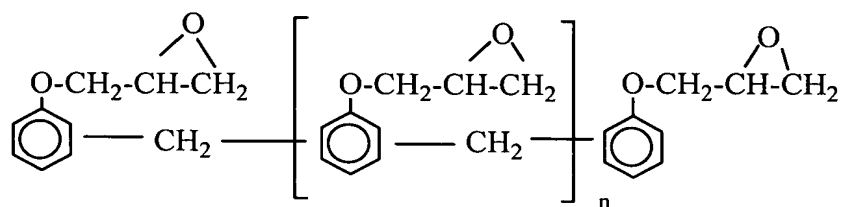
wherein each said EPOXY, independently, of said miscible toughener is



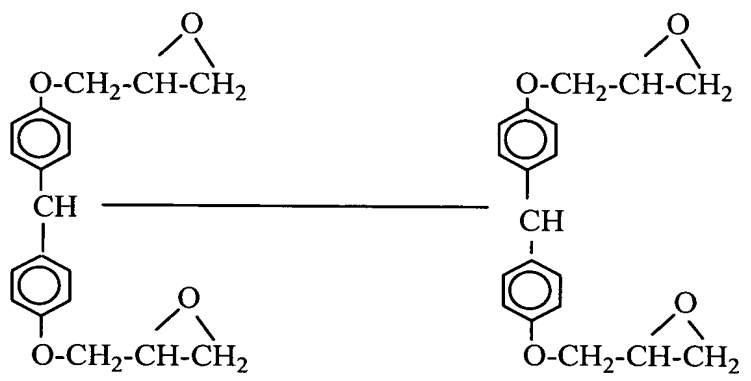
wherein n is an integer from 0 or about 0.1 to about 18, or;



wherein n is from 0 or 0.1 to about 18, or



wherein n is from about 0.0 to about 8; or



or combinations thereof; and

5 wherein said miscible toughener exists as a discontinuous phase in said crosslinked composition.

20. The composition of claim 16, which has a shelf stability life of at least two months before cure.

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21. The composition of claim 17, which has a shelf stability life of at least two months before cure.

22. The composition of claim 17, which has a shelf stability life of at least four months before cure.

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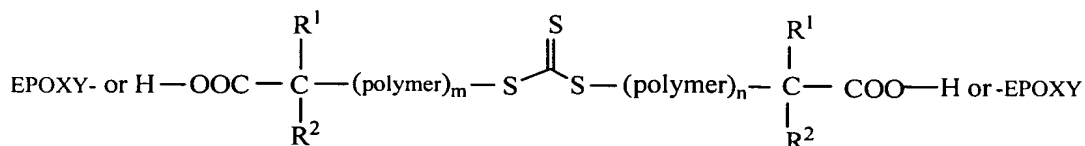
23. The composition of claim 18, which has a shelf stability life of at least four months before cure.

24. The composition of claim 18, which has a self stability life of at least six months before cure.

20

25. The composition of claim 19, which as a self stability life of at least six months before cure.

- 5 26. A composition comprising:
 a blend of a thermosettable resin and a toughener polymer or copolymer;
 said thermosettable resin being the reaction product of a polyepoxide
 having an average of more than one epoxide group per molecule with an
 unsaturated monocarboxylic acid, or an epoxidized polydiene rubber polymer or
 10 copolymer with an unsaturated monocarboxylic acid,
 said toughener polymer having the formula



Formula X¹

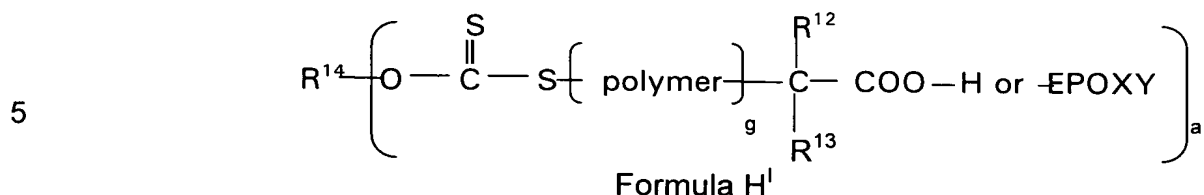
- wherein R¹ and R², independently, are an alkyl having 1 to about 6 carbon
 15 atoms, an alkyl having from 1 to 6 carbons atoms and 1 or more substituents, at
 least one aryl, or at least one substituted aryl having from 1 to about 6
 substituents on the aryl ring, and wherein said one or more substituents,
 independently, comprises an alkyl having from 1 to 6 carbon atoms, or an aryl, or
 a halogen group, or a cyano group, or an ether having a total of from 2 to about
 20 20 carbon atoms, or a nitro group, or combinations thereof,

 wherein m and n, independently, is a repeat unit of from about 5 to about
 1,000;

- wherein each said (polymer), independently, comprises a polyacrylate or
 polymethacrylate derived from an alkyl acrylate or alkyl methacrylate
 25 monomer wherein said alkyl has from 1 to about 18 carbon atoms, a
 polymer derived from a vinyl substituted aromatic monomer containing from
 8 to about 12 carbon atoms, a polymer derived from a conjugated diene
 monomer containing from 4 to about 12 carbon atoms, a polymer derived
 from acrylonitrile, or combinations thereof, or

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said toughener polymer having the formula



10 wherein R¹² and R¹³, independently, can be the same or different, can be a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R¹² and R¹³ can form or be a part of a substituted or unsubstituted cyclic ring having from 3 to about 12 carbon atoms;

15 wherein R¹⁴ is optionally substituted, and can be a linear or branched alkyl having from 1 to about 12 carbon atoms, an aryl group optionally saturated or unsaturated; an arylalkyl having from about 7 to about 18 carbon atoms; an acyl group; an alkene group; an alkenealkyl having from 3 to about 18 carbon atoms; an alkylene group; an alkoxyalkyl; derived from a polyalkylene glycol; derived from a polyalkylene glycol monoalkyl ether having from about 3 to about 200 carbon atoms; derived from a
20 polyalkylene glycol monoaryl ether having from about 3 to about 200 carbon atoms, a polyfluoroalkyl; a phosphorous containing alkyl; or a substituted or unsubstituted aryl ring containing heteroatoms;

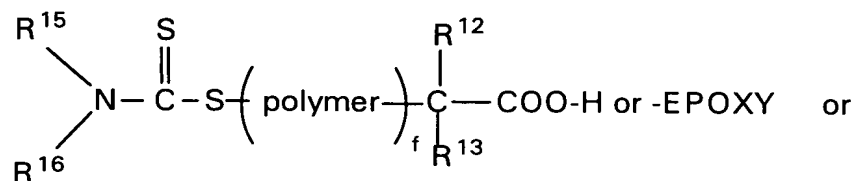
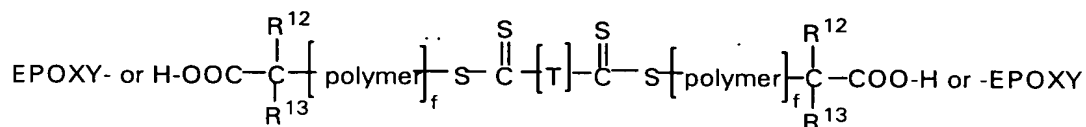
25 wherein said (polymer) is derived from at least one conjugated diene monomer, or a vinyl containing monomer or combinations thereof, with the proviso that each polymer repeat unit can be the same or different;

wherein said g is from about 1 to about 10,000; and

wherein said "a" is 1 to about 4; or

said toughener polymer or copolymer being a dithiocarbamate having the formula:

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Formula F^IFormula G^I

5 wherein each R¹² and R¹³, independently, is the same or different, is optionally substituted, and is a linear or branched alkyl having from 1 to about 12 carbon atoms; or an aryl group having from 6 to about 18 carbon atoms, optionally containing heteroatoms; or R¹² and R¹³ can form and be
10 carbon atoms;

 wherein R¹⁵ and R¹⁶, independently, is the same or different, optionally substituted, optionally contains heteroatoms, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbons; or an aryl group having from 6 to about 18 carbon atoms, optionally saturated or unsaturated; or an
15 arylalkyl having from 7 to about 18 carbons; or an alkenealkyl having from 3 to about 18 carbon atoms; or derived from polyalkylene glycol ether; or derived from an amine; or R¹⁵ and R¹⁶ are in the form of a substituted or unsubstituted cyclic ring with the nitrogen atom having a total of 4 to about 12 carbon atoms;

20 wherein T is a divalent radical having a nitrogen atom directly connected to each carbon atom of the two thiocarbonyl groups;

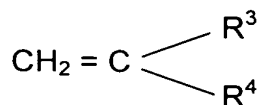
 wherein said (polymer) repeat units are derived from at least one conjugated diene monomer, or a vinyl containing monomer, or combinations thereof, with the proviso that each repeat unit can be the same or different;
25 and

wherein the number of said repeat units f , independently, is from 1 to about 10,000.

27. A composition according to claim 26,

wherein in said thermosettable resin said polydiene rubber polymer is derived from a conjugated diene monomer having from 4 to about 12 carbon atoms, and wherein said polydiene rubber copolymer is derived from a conjugated diene having from 4 to 12 carbon atoms and acrylonitrile,

wherein said Formula H¹ conjugated diene monomer has from 4 to 12 carbon atoms, and wherein said vinyl containing monomer has the formula:



wherein R^3 comprises hydrogen, halogen, $\text{C}_1 - \text{C}_4$ alkyl, or substituted $\text{C}_1 - \text{C}_4$ alkyl wherein said substituents, independently, comprise one or more hydroxy, alkoxy, aryloxy(OR^5), carboxy, acyloxy, aroyloxy(O_2CR^5), alkoxy-carbonyl(CO_2R^5), or aryloxy-carbonyl; N-pyrrolidonyl;

wherein R^4 comprises hydrogen, R^5 , CO_2H , CO_2R^5 , COR^5 , CN , CONH_2 , CONHR^5 , O_2CR^5 , OR^5 or halogen; and

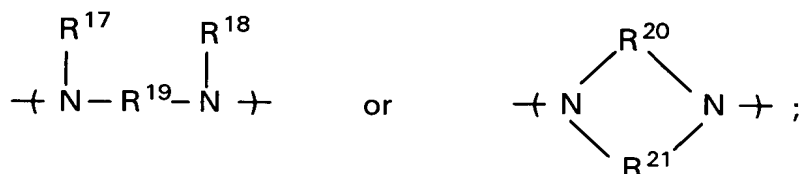
wherein R^5 comprises $\text{C}_1 - \text{C}_{18}$ alkyl, substituted $\text{C}_1 - \text{C}_{18}$ alkyl, $\text{C}_2 - \text{C}_{18}$ alkenyl, aryl, heterocyclyl, aralkyl, or alkaryl, and wherein said substituents, independently, comprise one or more epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy, (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, dicyanato, cyano, silyl, halo or dialkylamino, and

wherein g is from about 3 to about 5,000; or

wherein in said Formula F¹ and G¹, toughener polymer or copolymer f is from about 3 to about 5,000;

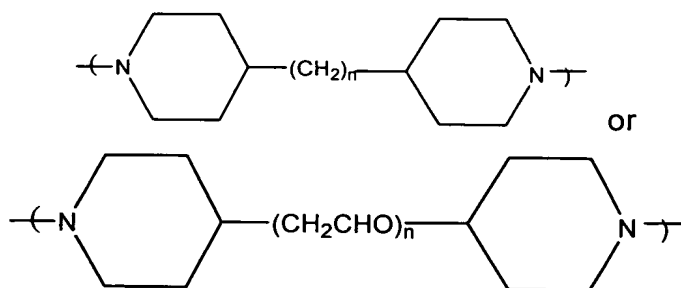
wherein T is:

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wherein R^{17} and R^{18} , independently, is the same or different, is optionally substituted, and is hydrogen; or a linear or branched alkyl having from 1 to about 18 carbon atoms; or an aryl group having from about 6 to about 18 carbon atoms; or an arylalkyl having from 7 to about 18 carbon atoms; or a alkenealkyl having from 3 to about 18 carbon atoms; wherein R^{19} is optionally substituted, or is non-existent; or an alkylene group having from 1 to about 18 carbon atoms; or derived from a polyalkylene glycol either having from 3 to about 200 carbon atoms; wherein R^{20} and R^{21} , independently, is the same or different, and is optionally substituted, and is an alkylene group having from 1 to about 4 carbon atoms, or

wherein T is:



wherein n is 0 to about 18.

28. A composition according to claim 27, wherein in said thermosettable resin said diene rubber polymer or copolymer, independently, is derived from butadiene, isoprene, piperylene, methyl pentadiene, or dimethylhexyladiene, or combinations thereof, and wherein each said monounsaturated acid, independently, is acrylic acid, methacrylic acid, crotonic acid, cinnamic acid or combinations thereof; and

wherein each said EPOXY, independently, of said toughener is derived from a: polyhydric phenol polyether alcohol; glycidyl ether of a novolac resin;

phenolic novolac epoxy, tetraphenylethane epoxy, glycidyl ether of mononuclear di- and trihydric phenol; glycidyl ether of bisphenol; glycidyl ether of polynuclear phenol; epoxy resin derived from diphenolic acid; glycidyl ether of aliphatic polyol; glycidyl ester; glycidyl epoxy containing nitrogen; glycidyl derivative of cyanuric acid; glycidyl resin derived from melamine; glycidyl amine; thioglycidyl resin; silicon-glycidyl resin; fluorine glycidyl resin; epoxy resin which is synthesized from monoepoxy other than epichlorohydrin including an epoxy resin derived from unsaturated monoepoxy; epoxy resin derived from monoepoxy alcohol; epoxy resin derived from monoepoxy by ester interchange; epoxy resin derived from glycidaldehyde; polyglycidyl compound containing unsaturation; epoxy resin which is synthesized from olefin and chloroacetyl; or an epoxy-resin adduct of the above, or combinations thereof;

and wherein m and n, independently, of Formula X^I is from about 70 to about 150, and wherein R¹ and R² are methyl.

29. A composition according to claim 28, wherein in said thermosettable resin said diene polymer is derived from butadiene and said diene copolymer is derived from butadiene and acrylonitrile, wherein each said unsaturated acid, independently, is acrylic acid or methacrylic acid,

wherein each said (polymer), independently, of Formula X^I is said polyacrylate and said polyacrylate is derived from ethyl acrylate, butyl acrylate, or ethyl-hexyl acrylate, or combinations thereof;

wherein, independently, each said polymer repeat unit, independently, of Formula H^I is derived from alkyl acrylate, vinyl acetate, acrylic acid, styrene, N-vinyl pyrrolidone, or a combination thereof, or

wherein R¹² and R¹³, independently, are an alkyl having from 1 to about 4 carbon atoms, or are part of a cyclic ring, and

wherein "a" is 2, and wherein R¹² and R¹³, independently, are a phenyl group or alkyl group having 1 to about 10 carbon atoms, or R¹² and R¹³ are part of a cyclic ring; or

36. The composition of claim 32, which is crosslinked.

37. The composition of claim 33, which is crosslinked.